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Nonlinear optical properties of one-dimensional organic molecular aggregates in nanometer films

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Abstract

Nanometer films of molecular J-aggregates of pseudoisocyanine (PIC) with various degrees of both static and dynamic disorder were prepared. The amount of static disorder was varied by modifying the local environment of the J-aggregates in the films, while the dynamic disorder was varied by changing the film temperature. Through these variations, the delocalization length N_{del} of the excitons was controlled, as could be monitored from the width of the exciton absorption line. This has allowed us to establish the scaling of the nonlinear optical susceptibility per aggregate molecule, $\chi^{(3)}/N$, with the delocalization length as $\chi^{(3)}/N \propto N_{\text{del}}^{\gamma}$, with $\gamma = 2.3 \pm 0.2$. This behavior turned out to be independent of the detailed nature of disorder, and agrees very well with the theoretically predicted size-enhancement of the cubic susceptibility in J-aggregates.

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During the past decade, materials and devices that enable a fast rate of optical signal processing have become a research area of great interest. These materials should combine a short relaxation time with a high optical nonlinearity. In this context, molecular J-aggregates have aroused much interest, as they possess a giant nonlinear optical susceptibility with picosecond relaxation times [1]. J-aggregates are one-dimensional chains of organic dye molecules, whose optical properties may be described by a Frenkel exciton model. The unique properties of J-aggregates derive from the delocaliza-

tion of the Frenkel excitons over many molecules of the aggregate. For perfectly ordered aggregates the exciton wave functions are entirely delocalized and the delocalization length N_{del} is determined by the physical size of the aggregate $N_{\text{del}} = N$. In reality, perturbations, such as impurities, thermal fluctuations, disorder in site positions, and inequivalence of the molecules constituting the aggregate caused by variation in the local environment, are sources of disorder that break the translational symmetry. As a result, the exciton wave functions localize on a part of the aggregate, with a typical size (for the optically dominant excitons) denoted $N_{\text{del}} \ll N$. A supralinear scaling of the cubic optical nonlinearity $\chi^{(3)}$ with the exciton delocalization size (so-called size-enhance-

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ment) has been theoretically predicted for ordered aggregates [2] as well as for aggregates with static diagonal disorder [3]. However, the nature of the extremely high nonlinearity of J-aggregates and its relation with the exciton delocalization length has thus far not been tested experimentally. In this paper, we report on such an experimental study, using various methods to vary and control the disorder, i.e. the delocalization length, in the aggregates.

Thin films (30×30 mm) of J-aggregates of pseudoisocyanine (PIC) were prepared on glass substrates by spin-coating from a PIC dye solution with concentration $c = 5 \times 10^{-3}$ M (a mixture of acetonitrile and ethylene dichloride with a volume ratio of 1:2 was used as solvent). The film thickness ($l \approx 15/40$ nm) was measured by spectral ellipsometry with an accuracy of 0.5 nm. In order to vary and control the degree of disorder in the samples, various amounts of an organic salt were added to the PIC solution as buffer particles. As salt we used either *N*-alkyl-quinaldinium iodide ($C_{12}H_{14}NI$) or tetrabutylammonium iodide ($(C_4H_9)_4NI$). Increasing the concentration of buffer particles is expected to decrease the static disorder in the aggregates. The reason is that this increase modifies the local environment of the aggregate from the very inhomogeneous environment constituted by the other aggregates to the more homogeneous environment of the buffer particles.

Typical absorption spectra of the thus obtained J-aggregate films at room temperature are shown in Fig. 1a. The prominent narrow peak at 576 nm corresponds to the resonance absorption line of the Frenkel excitons, the peak at 550 nm corresponds to

the absorption of isolated PIC dye molecules which did not form aggregates. The exciton absorption linewidth W (half width at half maximum) was found to decrease from 200 to 115 cm^{-1} when buffer particles were added and the concentration ratio of buffer and PIC was increased up to 4:1 (see Fig. 1b). This confirms the above expectation that adding the salt gives rise to better ordered aggregates, with a larger exciton delocalization length.

Assuming that the linewidth of the exciton absorption line is dominated by static disorder, W may be used to estimate the exciton delocalization length in our samples. The idea is based on scaling relations established in [4,5] of the typical separation between the lowest two exciton states on one localization segment, the exciton delocalization size, and W . The numerical simulations of [4] established the relation:

$$N_{\text{del}} = \frac{1}{1.12} \left(\sqrt{\frac{3\pi^2 |\omega_{\text{agg}} - \omega_{\text{mon}}|}{2W}} - 2.86 \right), \quad (1)$$

where, ω_{agg} and ω_{mon} are the resonance absorption frequencies for the aggregated and isolated molecules, respectively.

The imaginary part of the third-order nonlinear optical susceptibility of the J-aggregate films at room temperature was measured by the Z-scan technique [6]. The measurements were carried out with a pulsed dye laser (pulse duration 5 ns) tuned to the exciton absorption resonance. The incident radiation intensity was $I \approx 1 \text{ MW cm}^{-2}$. The absolute values of the nonlinear susceptibility were $\chi^{(3)} \approx 10^{-5}$ esu. In order to compare experimental data for different films, the values of the nonlinear susceptibility were

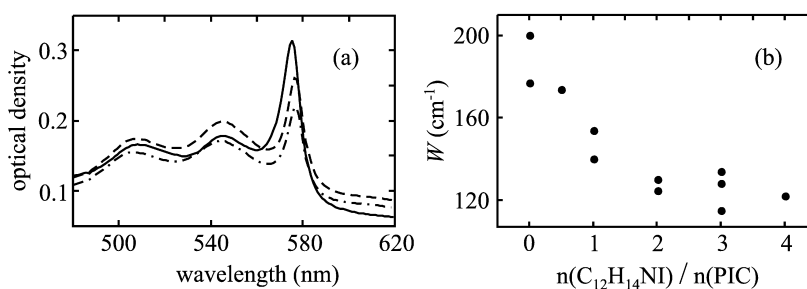


Fig. 1. Linear absorption spectra of the prepared J-aggregate films; (a) solid line, molar concentration ratio of $C_{12}H_{14}NI$ and PIC 1:1; dashed line, 2:1; dash-dotted line, 4:1. (b) The half width at half-maximum of the exciton absorption line of J-aggregates vs. molar concentration ratio of $C_{12}H_{14}NI$ and PIC.

normalized for (i.e. divided by) the concentration of PIC molecules that occur in the aggregate phase. This concentration is proportional to the ratio σ/l , where σ is the area under the exciton absorption line, and l is the film thickness. The normalized values of the imaginary part of the nonlinear susceptibility, $\chi^{(3)}/N$, have been plotted against the absorption linewidth on a double logarithmic scale in Fig. 2a. The solid line represents the best linear fit and has a slope $\delta = -1.58 \pm 0.15$, corresponding to the power dependence $\chi^{(3)}/N \propto W^\delta$.

Using Eq. (1), one can translate this scaling into a relation between the experimentally measured values of the nonlinear susceptibility and the delocalization length: $\chi^{(3)}/N \propto N_{\text{del}}^\gamma$ with $\gamma = 2.3 \pm 0.2$. It should be noted that this power scaling agrees very well with the theoretical prediction of $\gamma = 2.36$ for the size-enhancement in one-dimensional aggregates with static diagonal disorder [3].

The modification of the local aggregate environment using buffer particles influences the static disorder in the J-aggregate films. As an alternative, we have used temperature variation to control the dynamic disorder. In particular, we have done experiments at 293 and 80 K. The absorption line width W for the series of J-aggregate films turned out to decrease with temperature from the range 140–210 cm^{-1} at room temperature to 70–130 cm^{-1} at 80 K. This behavior reflects the expected decrease of dynamic disorder and the concomitant increase of the exciton delocalization (or coherence) length.

The nonlinear susceptibility of the J-aggregate films was measured using the pump-probe technique at 293 and 80 K. The experiment was carried out

with two pulsed dye lasers (pulse duration 5 ns). The intensity of the pump radiation was $0.5/1 \text{ MW cm}^{-2}$, while the intensity of the probe radiation was less by three orders of magnitude. The pump and probe pulses acted on the sample simultaneously. For each sample, the frequency of both the pump and probe radiation was tuned to the exciton absorption resonance. The absolute values of the nonlinear susceptibility $\chi^{(3)}$ were about 10^{-5} esu at 293 K and 10^{-4} esu at 80 K.

The normalized values of the thus obtained nonlinear susceptibility versus the absorption linewidth are shown on a double logarithmic scale in Fig. 2b. The solid line represents the best linear fit and has a slope $\delta = -1.36 \pm 0.2$, corresponding to the power dependence $\chi^{(3)}/N \propto W^\delta$. Using Eq. (1), we now obtain for the scaling of the nonlinear susceptibility with the delocalization length: $\chi^{(3)}/N \propto N_{\text{del}}^\gamma$ with $\gamma = 2.2 \pm 0.3$. Again this result is in good agreement with the theoretical prediction of [3] ($\gamma = 2.36$). This is all the more remarkable, as we have not only influenced the static disorder, but the dynamic disorder as well. The theoretical prediction does not account for dynamic fluctuations. The results suggest that the dynamic disorder may be understood as being quasi-static on the scale of exciton motion.

In conclusion, we have found power-law scalings of $\chi^{(3)}$ with N_{del} (or of $\chi^{(3)}$ with W) that do not depend on the way used (static or dynamic) to influence the amount of order in the films. The scaling law that we found agrees very well with the theoretical prediction for the size-enhancement of the cubic susceptibility in molecular J-aggregates with static disorder [3]. The results constitute a clear

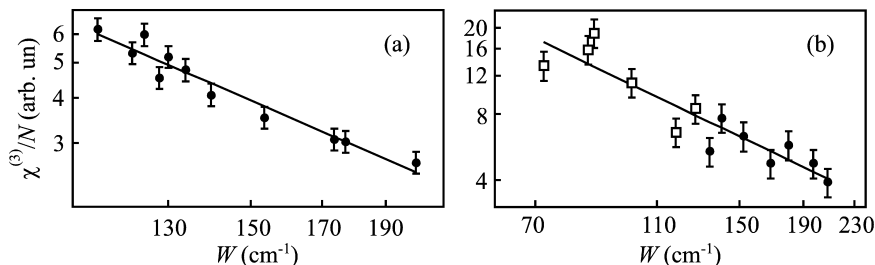


Fig. 2. Normalized values of imaginary part of the cubic optical susceptibility vs. the absorption linewidth (double logarithmic scale). (a) Data measured using the Z-scan technique at room temperature for a series of samples with addition of *N*-alkyl-quinaldinium iodide salt, (b) data measured using the pump-probe technique at room temperature (solid dots) and nitrogen temperature (open squares) for a series of samples with addition of tetrabutylammonium iodide salt.

experimental demonstration that exciton delocalization indeed underlies the giant nonlinear optical susceptibilities observed for J-aggregates.

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